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ATMOSPHERIC MEASUREMENTS, MONITORING, AND MODELLING OF ACID FORMING EMISSIONS

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Abstract

The status of the measurement, monitoring and modelling of acid forming emissions in Alberta is reviewed in the context of managing an integrated environmental system. The need for sensitive sampling methods for use in studies such as the Acid Deposition Research Program is apparent, and one such system, the Kananaskis Atmospheric Pollutant Sampler (KAPS), is described and preliminary results presented. Future thrusts in the areas of measurement, monitoring, modelling and management of importance to Alberta are outlined.

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1. INTRODUCTION

The emissions of sulphur dioxide and nitrogen oxide from all sources in Alberta during 1982 amounted to about 488 000 and 353 000 tonnes respectively. These primary emissions may be deposited in the ecosystem directly, or be converted to secondary air pollutants, prior to deposition. In order to understand the physical, biological and health effects of these pollutants it is necessary to measure, monitor and model atmospheric diffusion, transport, transformation and deposition processes.

The words "measure, monitor, and model" are intimately connected, and have specific meaning in atmospheric sciences. Measurements are determinations of the amount of an atmospheric pollutant present, and are made over a limited period of time using simple or sophisticated methods. Monitoring consists of continuous or periodic measurements over a long period to meet long term objectives; for example to define trends, to check on compliance with standards/ guidelines or to study relationships among variables. Modelling refers to numerical techniques or methodologies, based upon physical principles, for estimating pollutant concentrations and depositions in space and time as a function of the emission distribution and the attendant meteorological and geophysical conditions.

A complete literature review on atmospheric measurements, monitoring and modelling is beyond the scope of this paper. Recent reviews have covered measurement and monitoring activities in North America including general processes (Fowler 1984), dry deposition (Sehmel 1980) and worldwide modelling activities (Weber 1982; Fronza and Melli, 1982; Canada-U.S. MOI Final Reports, 1982). This paper outlines the interacting components of an environmental system, examines Alberta studies, describes current activities and identifies additional informational needs.

2. AN INTEGRATED ENVIRONMENTAL SYSTEM

Any phenomenon that involves the interaction between two or more components can be called a system. An integrated environmental

system linking air pollutant emissions to environmental effects is depicted in Figure 1. Each of the three systems is subject to the four activities of measurement, monitoring, modelling and management. For instance, measurements are used to test models, which are used to do interpolations and extrapolations, and in turn are used for making management decisions. The decisions may prompt further measurements, and the cycle is repeated as often as necessary to achieve the desired end results. In some circumstances, not all of the activities are required. Measurements, monitoring data and modelling forecasts are inputs to management, and in turn, are affected by management.

A model is an abstraction, or simplification, of a system. It serves to formalize knowledge by integrating observations and theories, and to test our understanding of the processes involved. A model can predict hypothetical future states of a system or reconstruct past states that were not observed. The model goes beyond known circumstances and allows the study of a system under conditions that we are not yet able to observe or create, or may never be able or desirous of observing or creating. It may yield information about the behaviour of the complete system that is not obvious from the knowledge of individual parts, and can generate hypotheses for further testing. The interplay of model and empiricism in alternating series is a most powerful scientific tool. Once forecasts are available, it then becomes possible to study alternative actions; that is, assess competing scenarios required to make management decisions. For example, resources can be allocated in various ways to optimize chosen conditions within the system.

3. MEASUREMENTS AND MONITORING

3.1 STANDARD METHODS

3.1.1 Gaseous Pollutants

Techniques for the measurement and monitoring of ambient concentrations of the most common gaseous atmospheric pollutants (SO_2, H_2S, NO, NO_2, O_3 and CO) are well established and are used extensively by industrial and government monitoring networks in Alberta,

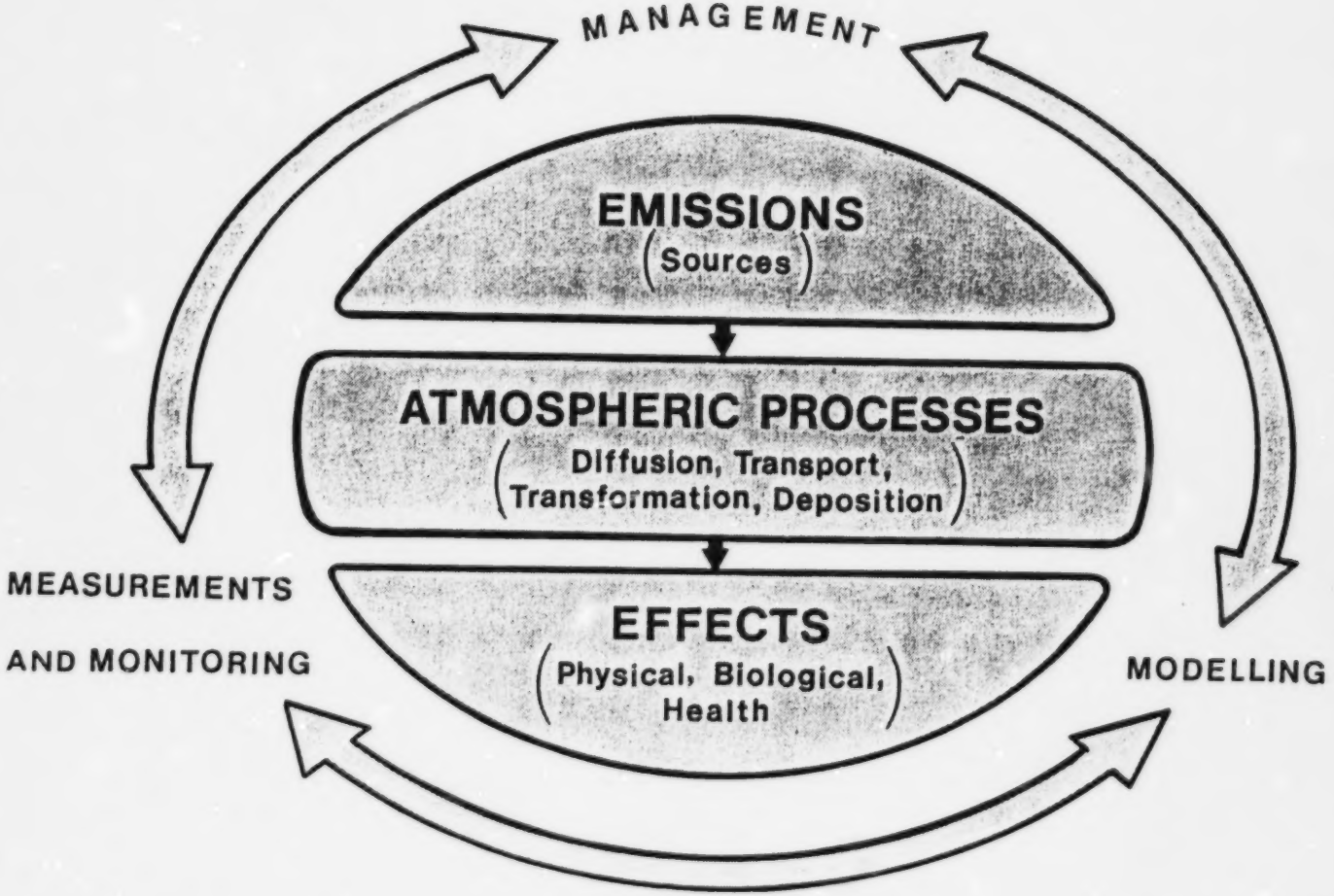

Figure 1. An integrated environmental system.

as well as for research programs within the Province. A review of these activities is beyond this paper, but some examples are:

1. The network of nine comprehensive and continuous air monitoring stations used by Alberta Environment to monitor urban air quality.
2. The Strathcona Industrial Compliance Network developed by an association of ten industrial plants to monitor air quality in the eastern portion of the City of Edmonton and the adjacent area of the County of Strathcona (Docken et al. 1985).
3. A number of networks operated by private companies to monitor air quality in the vicinity of major industrial operations. These networks generally monitor H_2S, SO_2, wind speed, and wind direction, and consist of three to five air quality monitoring trailers.
4. The extensive baseline information on air, precipitation and other environmental parameters obtained in northeastern Alberta by the Alberta Oil Sands Environmental Research Program (AOSERP), Suncor and Syncrude.
5. The West Whitecourt Case Study, an interdisciplinary research program to determine the consequences of chronic exposure of the forest ecosystem to low concentrations of sulphur gas emissions (Legge et al. 1981).
6. The heavily instrumented monitoring sites of the Acid Deposition Research Program, which continuously monitor seven gaseous pollutants and intermittently monitor four others. Eleven meteorological parameters are also monitored and particles and precipitation are collected for subsequent chemical analysis. Two sites are located near Crossfield, Alberta and the third, a background air quality monitoring station, is situated at the Fortress Mountain ski area in the Kananaskis Valley. These stations are to provide air quality information for use in assessing the possible impacts of industrial emissions on air, water, land and human systems.

3.1.2 Aerosols

Atmospheric aerosols fall into two main categories: (1) large particles of greater than 1.0 μm diameter, derived from the earth's crust and reflecting its composition, and (2) particles emitted with or generated from gaseous emissions and generally in the size range of 0.1 to 1.0 μm, the accumulator mode. These particles consist largely of ammonium nitrate and ammonium sulphate, but include sulphuric acid, which exists as an aerosol.

The monitoring of atmospheric aerosol concentrations is ususally carried out on an integrated basis, often with 24 h of sample collection, rather than on a real-time, continuous basis. Particles are collected on a filter medium and weighed, and may also be analyzed for chemical composition. Particles can be separated into two size fractions, with the cutoff point being 2.5 μm. The smaller-sized fraction in this dichotomous sampling is of interest from the point of view of acidity, as it may contain sulphuric acid. In Alberta, dichotomous samplers are operated in Calgary and Edmonton as part of the Canadian National Air Pollution Surveillance (NAPS) network. Samples are collected for 24 h every sixth day, on the same schedule as high volume sampling. The weights of material collected and the nitrate and sulphate concentrations are determined.

3.2 NON-STANDARD METHODS

Although nitric acid is believed to be a major contributor to acidity, no standard method presently exists for the routine measurement of nitric acid in the atmosphere. The sampling system most frequently used is a dual filter pack consisting of a Teflon front filter to collect particles, followed by a nylon filter to collect gaseous nitric acid. The filters are then analyzed for nitrate by ion chromatography. In an intercomparison of methods, Spicer et al. (1982) found that the dual filter system overestimated nitric acid because particulate ammonium nitrate is volatilized from the Teflon filter and collected on the nylon filter. The method does, however, provide an excellent measure of total nitrate (Grosjean 1983).

This method was used to study nitric acid and particulate nitrate concentrations in the ambient atmospheres of Calgary and Edmonton, and at a background site in the Kananaskis Valley, 70 km west of Calgary. Mean concentrations of inorganic nitrate in Calgary during the summer of 1980 were low, 0.51 $\mu g \cdot m^{-3}$, of which 0.26 $\mu g \cdot m^{-3}$ was volatile nitrate (nitric acid plus volatized ammonium nitrate). During the period November 1982 to October 1983 in Edmonton, mean total nitrate was 1.16 $\mu g \cdot m^{-3}$ of which 0.30 $\mu g \cdot m^{-3}$ was volatile nitrate. The highest volatile nitrate concentration was 2.36 $\mu g \cdot m^{-3}$. These total nitrate concentrations were somewhat lower than those recorded in Toronto in 1979 (Barrie et al. 1981). Background mean volatile nitrate concentrations recorded in the Kananaskis Valley in August 1980 were 0.22 $\mu g \cdot m^{-3}$, with total nitrate being 0.35 $\mu g \cdot m^{-3}$ (Peake et al. 1983, 1985).

3.3 THE KANANASKIS ATMOSPHERIC POLLUTANT SAMPLER (KAPS)

A sampling system developed and tested by the Kananaskis Centre for Environmental Research at the University of Calgary provides a method for collecting an integrated sample of gases and of aerosols that is free from many of the shortcomings of the earlier methods. Acid gases, ammonia and particles are collected separately and there is no reaction of gases to change the composition of particles. Nitric acid is collected without interference from volatile ammonium nitrate.

This system was developed as part of a study of acid deposition in Alberta (ADRP, the Acid Deposition Research Program). The heart of the system is the annular denuder tube developed by Possanzini et al. (1983). In the Kananaskis Atmospheric Pollutant Sampler (KAPS) system, the annular denuders are utilized to capture acid gases, primarily nitric acid, nitrous acid and sulphur dioxide, as well as ammonia, for subsequent analysis by ion chromatography or colorimetrically. The design of the KAPS system is shown in Figure 2. Three annular denuder tubes are connected in series. Each denuder tube consists of an outer glass tube having a three-quarter inch outside diameter and a 13.2 mm inside diameter, and an inner tube of 10.0 mm outside diameter. The annulus walls of the first denuder tube (G) are coated with sodium carbonate and retain nitric acid, nitrous acid,

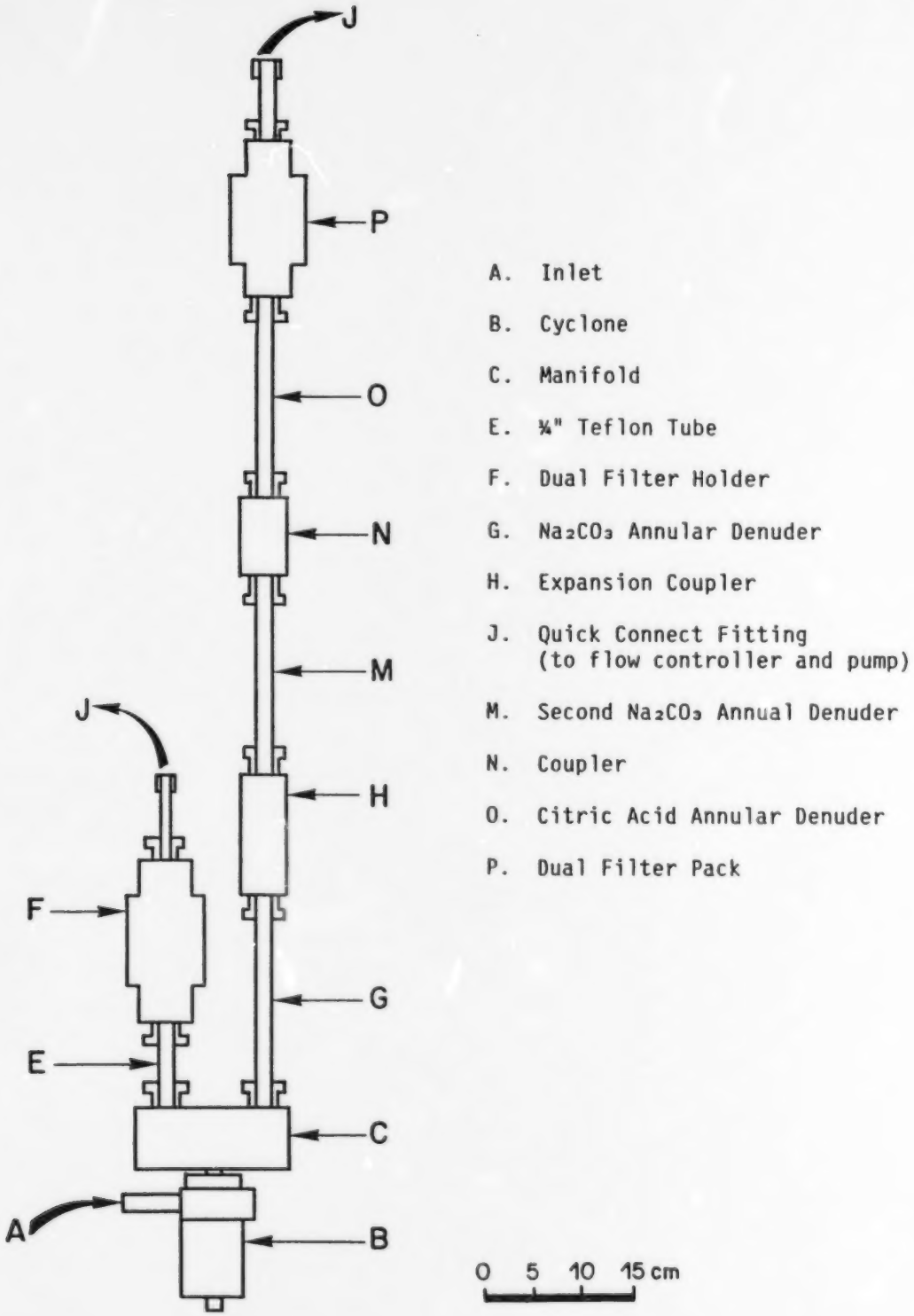

Figure 2. The Kananaskis Atmospheric Pollutant Sampler (KAPS).

sulphur dioxide and other acid gases. The tube also retains some nitrous oxide (about 5%), which interferes in the subsequent analysis of nitrous acid by ion chromatography. Some particles may also be deposited in the tube, but their effect is likely to be negligible as laminar flow is maintained in the sampling system. The second denuder tube (M) retains some of the remaining nitrous oxide (a further 5%), and is used to correct the nitrous acid value as determined from analysis of nitrite in the first denuder tube. The third denuder tube (O) is coated with citric acid, and is used to collect ammonia. The system has been tested extensively in both laboratory and field trials, including tests in California, and has proven effective for the collection of acid and basic gases.

Of particular interest is the ability of the KAPS system to collect nitrous acid. Measurements carried out in Calgary during the period June 24 to June 28, 1985, showed nitrous acid to be generally more abundant than nitric acid, whereas, during the period July 2 to July 7, nitric acid was usually dominant. Nitrous acid concentrations ranged from 0.05 $\mu g \cdot m^{-3}$ to 1.24 $\mu g \cdot m^{-3}$, and nitric acid concentrations from 0.04 $\mu g \cdot m^{-3}$ to 1.05 $\mu g \cdot m^{-3}$. Nitrous acid to nitric acid ratios varied greatly, from 0.18 to 14, and there were strong diurnal variations.

Measurements of nitrous acid in other urban atmospheres are scarce but concentrations of up to 2.4 $\mu g \cdot m^{-3}$ were found by Sjodin and Ferm (1985) in Gothenburg, Sweden.

In Calgary, SO_2 was more abundant than nitric and nitrous acids, with mean daily concentrations ranging from 0.52 $\mu g \cdot m^{-3}$ to 3.17 $\mu g \cdot m^{-3}$. During the period June 26 to July 6, ammonia was collected in Calgary using a citric acid annular denuder tube. Ammonia concentrations ranged from 1.9 $\mu g \cdot m^{-3}$ to 14.5 $\mu g \cdot m^{-3}$.

The KAPS system also collects fine particles for chemical analysis. Large particles such as windblow dust are removed by a Teflon cyclone, and fine particles are collected on a Teflon filter. The cut-off point between the coarse and fine particles varies as a function of the desired sampling rate, but generally is maintained at 2.0 μm. The KAPS system offers an advantage over standard filter

packs as the particles collected on the filter medium are not subject to reactions with acid gases or ammonia because these gases have been previously removed by the annular denuder tubes.

Three sophisticated air monitoring trailers equipped with KAPS samplers are operated as part of the ADRP. Two are located near Crossfield, Alberta, and the third, a background air quality monitoring station, is located at the Fortress Mountain ski area in the Kananaskis Valley. Preliminary data are shown in Table 1.

3.4 WET AND DRY SULPHUR DEPOSITION IN ALBERTA

Five stations in the Canadian Network for Sampling Precipitation (CANSAP) are located in Alberta. In addition, six precipitation monitoring sites have been operated since 1978 by Alberta Environment. These networks monitor the chemical composition of rainfall primarily for the major anions, SO_4^{2-}, NO_2^- and Cl^-, and the major cations NH_4^+, Ca^{2+}, Mg^{2+} and K^+, which represent the principal ions (excluding hydrogen) in precipitation. Hydrogen ion concentration is measured as pH.

Precipitation samples have been collected from the relevant Alberta stations on a monthly basis since 1978, and average data are shown in Table 2. These data were examined for chemical composition, spatial distribution, seasonal variation, temporal trend, acidity and wet sulphate deposition (Lau and Das 1985). Alberta precipitation has an average pH of 5.5; calcium, sulphate and ammonium ions are the predominant species, and the higher ion concentrations occur in southern Alberta. The relatively high concentration of calcium indicates a contribution from wind-blown dust. The large amounts of precipitation in the summer result in a lower ion concentration in the rainfall. No temporal trend was apparent. The average wet sulphate deposition in Alberta from 1978 to 1984, based on this data, was 8.9 $kg \cdot ha^{-1} \cdot yr^{-1}$ (kilogram per hectare per year).

The acidic input to a receptor is derived from a combination of both wet and dry deposition. In the past, attention focussed on wet deposition, but the importance of dry deposition is now widely recognized. Dry deposition of gases and particles is estimated to be ten times greater than wet deposition in semi-arid areas of California (Liljestrand 1979).

Table 1. Concentrations of pollutants, collected with the KAPS system, at three Alberta locations (preliminary data, no blank correction) $\mu g \cdot m^{-3}$.

	PRIMARY GASES			SECONDARY GASES		PARTICULATES	
	NH_3	SO_2	NO_2*	HNO_2	HNO_3	NO_3^-	SO_4^{2-}
Background							
Mean	0.47	1.09	0.50	0.002	0.07	0.35	0.21
Std. Dev.	0.48	1.35	0.23	-	0.20	0.23	0.16
Minimum	0.01	0.11	0.21	0.000	0.01	0.05	0.01
Maximum	2.19	6.63	1.35	0.016	0.56	1.10	0.69
N	58	60	60	-	60	60	58
Site No. 1							
Mean	1.09	5.61	1.89	0.016	0.27	0.64	0.83
Std. Dev.	1.55	4.91	1.76	-	0.38	0.70	1.84
Minimum	0.00	0.34	0.15	0.000	0.00	0.07	0.05
Maximum	10.54	29.41	11.42	0.096	1.26	3.80	12.32
N	65	65	64	66	-	64	64
Site No. 2							
Mean	0.74	9.97	2.54	0.007	0.34	0.73	0.70
Std. Dev.	0.82	13.41	3.32	-	0.60	1.27	1.01
Minimum	0.03	0.27	0.41	0.000	0.05	0.00	0.04
Maximum	3.97	7.19	19.96	0.94	1.22	8.50	5.17
N	62	60	62	-	60	60	62

* by NO_x analyzer

Table 2. Volume-Weighted Averages of Parameters Measured for 1978-1984* (concentrations in μequivalents·ℓ$^{-1}$)

	pH	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}
Beaverlodge	5.17	28.9	10.0	25.8	35.3	8.8
Calgary	5.77	65.4	20.6	40.8	93.0	23.3
Coronation	5.46	39.3	16.6	15.7	32.3	8.7
Edmonton	5.45	39.0	16.1	29.6	26.1	10.9
Edson	5.61	31.6	8.6	8.2	33.5	7.1
Fort McMurray	5.26	38.4	11.6	3.4	59.5	31.3
Lethbridge	6.06	47.8	24.6	26.1	132.6	28.6
Red Deer	5.39	37.0	15.6	36.2	30.9	7.3
Rocky Mtn. House	5.53	39.1	11.8	20.6	41.9	11.4
Suffield	5.60	50.9	19.9	70.6	48.4	18.5
Whitecourt	5.71	41.9	12.8	11.5	93.0	19.5
OVERALL	5.48	41.1	14.7	25.2	55.3	14.8

* Alberta Environment stations 1978-1984 except for Calgary (1979-1984); CANSAP stations 1978-1983.

Measurements of tne relative amounts of wet and dry deposition in Alberta indicate that under our dry climatic conditions, dry deposition predominates by a factor of 5 (Caiazza et al. 1978; Legge et al. 1981). Walker et al. (1981) calculated that 7 to 9 $kg \cdot ha^{-1}$ of total sulphate S was deposited annually in a 4600 km^2 area, within which ten major sources were licensed to produce 330 tonnes S per day. At distances greater than 40 km from the sources, the deposition rate varied from 4 to 6 $kg \cdot ha^{-1}$.

One approach to determining dry deposition is to measure the ambient concentration of the species of interest and to multiply this by an appropriate deposition velocity. Deposition velocity depends on the wind speed, stability, topography, the type of ground cover, and surface wetness. Many of these dependencies are not easily quantified. Measurements by mass balance, eddy flux, eddy accumulation, or profile techniques give deposition velocities that range over four orders of magnitude for gases, and over three orders of magnitude for particles (Sehmel 1980).

A study of the deposition velocity of sulphur dioxide to a field of barley was carried out in 1983 near Crossfield, Alberta using the atmospheric flux method (Chadder et al. 1984). Results indicated SO_2 deposition velocities of approximately 0.1 $cm \cdot s^{-1}$ in the evening and 1.0 $cm \cdot s^{-1}$ during morning daylight hours. This is close to the same range as reported by Fowler (1984) for wheat, a maximum of 1.2 $cm \cdot s^{-1}$ during the day and a minimum of 0.2 $cm \cdot s^{-1}$ at night.
During the study, sulphur dioxide concentrations ranged from 0.2 to 116 $\mu g \cdot m^{-3}$ but generally were in the 5 to 30 $\mu g \cdot m^{-3}$ range.
Typical averaged values of deposition velocities as summarized by Denison et al. (1979) are: 0.3 $cm \cdot s^{-1}$ for snow, 0.6 $cm \cdot s^{-1}$ for soil, 1.1 $cm \cdot s^{-1}$ for grass, 1.1 $cm \cdot s^{-1}$ for water, and 1.6 $cm \cdot s^{-1}$ for forest. In a study of acid deposition in the Western United States Hidy and Young (1986) used mean deposition velocities of 0.5 $cm \cdot s^{-1}$ for SO_2, 0.2 $cm \cdot s^{-1}$ for SO_4^{2-}, 0.1 $cm \cdot s^{-1}$ for NO_2, 1.0 $cm \cdot s^{-1}$ for HNO_3 and 0.2 $cm \cdot s^{-1}$ for NO_3^{-1}. Using these velocities the estimated dry deposition of sulphate (sulphur dioxide and particulate sulphate) in rural and background areas of the Western United States is

7 $kg \cdot ha^{-1} \cdot yr^{-1}$, and of nitrate (nitrogen dioxide, nitric acid and particulate nitrate) is 5 $kg \cdot ha^{-1} \cdot yr^{-1}$.

The inability to monitor dry deposition or accurately determine deposition velocities leads to large uncertainties in the estimates of total deposition. This makes it difficult to assess the present situation and to conduct the effects research needed to establish target loadings. Because management decisions are founded on comparisons between actual and desirable states, these uncertainties must be reduced and appropriate standards established.

4. ATMOSPHERIC POLLUTION MODELLING

4.1 NATURE AND USES OF MODELS

An atmospheric pollution model comprises a number of modules or submodels that represent the major processes governing the behaviour of airborne pollutants (Fig. 3). The model is "mathematical" because it consists of equations that relate various dependent and independent variables within the preocess and between processes. Thus, a volume of pollutant is released (emission), carried by the wind (transport), spread out by turbulence (diffusion), reacted chemically with other species and sunlight (transformation) and removed from the air by vegetation and soil through precipitation, gravitational settling, impaction, electrical attraction, Brownian motion, chemical reaction and other surface collection mechanisms (deposition). In order to operate, a model must have a number of specific inputs obtained by processing the available measurements. The failure of outputs to compare favourably with actual measured concentrations or deposition can be caused by any of the components - input data, preprocessing algorithms, physical/chemical process models - or by the interaction between components. The lack of appropriate input data is a major impairment to model performance.

A decision-maker routinely faces a host of questions to which reasonable answers must be given quickly. Atmospheric pollution models allow the exploration of hypothetical situations and their consequences for air quality/deposition. Quantitative answers to "what if"

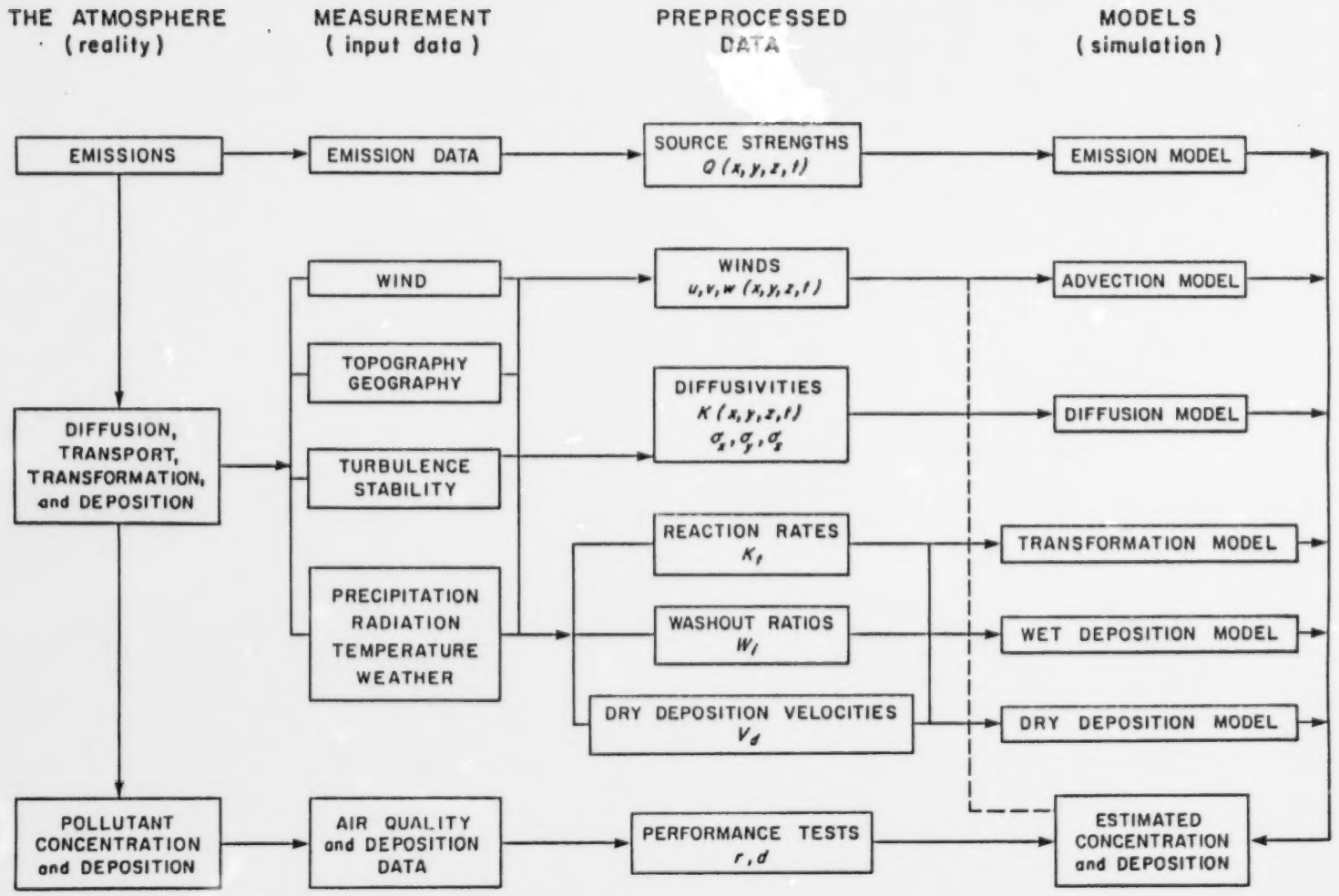

Figure 3. Flow scheme showing modules or elements in an atmospheric pollution model.

questions provide the foundation for decisions that govern many day-to-day activities. Such models are tools that decision makers employ to obtain some of the information that enters into their deliberations (Angle 1979). Some typical applications are summarized in Table 3.

4.2 MODELLING IN ALBERTA

4.2.1 Short Range (0 to 100 km)

The early work of Benjamin (1975) showed that at the "hot spot" (position of the maximum) downwind of a sour gas plant, the dry deposition flux could be between 10 and 100 times greater than the deposition flux occurring at a distance of 100 km. A value of about 2 $kg \cdot ha^{-1} month^{-1}$ (sulphur) was calculated at a distance of 3 km for a typical sour gas plant in July. He also calculated that about 25% of the sulphur in the plume would be deposited within 100 km. Model sensitivities drew attention to the need for better information on the heights and strengths of elevated inversions and the frequency of ground-based inversions.

Walmsley and Bagg (1977) used a modified version of the EPA Climatological Dispersion Model to estimate dry deposition around the Suncor oil sands plant. Maxima of about 16 $kg \cdot ha^{-1} \cdot yr^{-1}$ (sulphur) occurred 2 to 3 km SSE and NNW of the plant. As with Benjamin, a deposition velocity (ratio of deposition flux to ambient concentrations) of 1 $cm \cdot s^{-1}$ was used.

A model developed by Western Research (1978) allowed deposition velocity to be a function of atmospheric stability and incorporated wet deposition by the equilibrium scavenging theory. Wet deposition within 40 km of the source was found to be about one-tenth that of the dry, and the maximum total depositions were less than 6 $kg \cdot ha^{-1} \cdot yr^{-1}$ (sulphur).

Greater realism was added to this model by Alberta Environment (1984) incorporating, among other things, surface roughness, variable windspeed with height, and limited mixing. The annual deposition maxima for the small and medium sources were 5 to 10 km away from the source. The large source had a maximum 25 to 30 km away. The highest total deposition was found to be about 11 $kg \cdot ha^{-1} \cdot yr^{-1}$ of sulphur

Table 3. Air Pollution Model Applications

1. AIR POLLUTION IMPACT ANALYSIS

   - Existing sources
   - Plans involving changes in existing emission patterns
   - Government policies affecting emission patterns directly or indirectly
   - Alternative site selection (minimization of adverse impacts)

2. ATTAINMENT OF AIR QUALITY/DEPOSITION STANDARDS

   - Monitoring network design
   - Formulation of control policies
   - Licencing and regulation
   - Meteorologically controlled emission systems
   - Stack design

3. CHARACTERIZATION OF EXISTING AIR QUALITY/DEPOSITION IN MULTI-SOURCE AREAS (Analysis of ambient concentrations/depositions of primary and secondary pollutants)

   - Determination of spatial and temporal patterns
   - Hot spot identification
   - Worst case identification
   - Determination of source contributions
   - Separation of anthropogenic and natural causes
   - Data base error diagnosis (emissions inventory and monitoring)

4. HISTORICAL AIR QUALITY/DEPOSITION TREND ANALYSIS

   - Delineation of changes caused by changes in weather, source distribution and emissions
   - Selection of standards

5. SUPPORT FOR EFFECTS AND ECONOMIC STUDIES (Distribution and magnitude of concentrations/depositions)

for the medium source. The annual total deposition resulting from a large continuous flare (emission 10 t yr^{-1} was about half that associated with the medium gas plant. The total yearly sulphur deposition within a 100 km radius is about 24% of yearly sulphur emissions except for the large gas plant where the percentage is about 9%, due primarily to a very large plume rise and an associated penetration into the capping stable layer.

The frequency distribution model developed for the Alberta oil sands (Davison et al. 1981) uses more advanced boundary layer parameterizations to obtain concentration and deposition estimates. This model also has more powerful analyses capabilities than are available on traditional climatological models. The user can construct ground-level concentration statistics based upon user-selected criteria for inclusion/exclusion or weighting of time series realizations depending upon ambient meteorological conditions. In a recent comparison of model-predicted distributions and observed distributions (Nosal 1985), the Kolmogorov Smirnoff test showed no significant differences with 99% confidence. Such a model should prove useful in relating air quality to vegetation effects. The development of an environmental response model to link the atmosphere and the biosphere is one of the goals of the Acid Deposition Research Program.

Until quite recently, short-range transport and deposition models contained either no chemical transformations at all or simply fixed percentages per hour. Bottenheim and Strausz (1981) developed a chemically reaction plume model describing the homogeneous gas-phase chemistry of a plume containing SO_2 and NO_x from an oil sands extraction plant. The oxidation rate for SO_2 in typical summer conditions was found to rise almost linearly to $2\%\cdot h^{-1}$ within 60 minutes of travel time, and then to increase more slowly. The rate was also found to be sensitive to the ratio of in-plume NO_x to ambient hydrocarbons. Emitted NO_x was 90% converted into PAN and nitrate within four hours of travel time, whereas 10 to 18% of the SO_2 was converted to sulphate. These results compared favourably with available observations in the oil sands and elsewhere.

A detailed oxides of nitrogen conversion model was developed by Vet et al. (1982) to address the problem of NO_2 formation downwind of compressor stations. This model consisted of 38 reactions for the more generalized polluted atmosphere scheme of Bottenheim and Strausz (1978). Evaluation of this model against existing data is currently underway (Reid et al. 1985).

4.2.2 Medium Range (100 to 1000 km)

For the transport of material over larger distances, it is important to include the chemical transformations of sulphur dioxide to sulphate and the emission of sulphates. The LRTAP model TRANS includes this conversion chemistry and was used by the Oil Sands Environmental Study Group to assess the possible long-term impact of oil sands development (MEP 1982). The model also included nitrogen oxides emissions and subsequent nitrogen deposition. Weisman et al. (1982) reported that the long-term mean loading of sulphur had a peak value of 4.0 $kg \cdot ha^{-1}$ per year in the region of Fort McMurray, with the wet component contributing 40%. The loading dropped to 1 $kg \cdot ha^{-1}$ within 300 km of Fort McMurray. Of the wet deposition, 90% was due to sulphur dioxide and 10% to sulphates. Most of the SO_2 wet deposition occurred in winter, while most of the sulphate wet deposition occurred in the summer (MEP 1982).

The long-term loading of nitrogen (wet plus dry) showed a peak rate of 0.44 $kg \cdot ha^{-1} \cdot yr^{-1}$ as nitrogen. The mean loading of sulphur in the range of 0 to 100 km was 3.7 $kg \cdot ha^{-1} \cdot yr^{-1}$, with wet deposition accounting for 40% of the deposition. In the distance range of 300 to 500 km, the average total loading was only 0.24 $kg \cdot ha^{-1} \cdot yr^{-1}$ with wet loading accounting for 50%. It was also found that approximately 25% of the sulphur emissions are deposited within 200 km of the sources, 50% are deposited within the first 500 km and 75% within 1000 km. For nitrogen, the corresponding fractions are 21%, 42% and 60% of annual emissions.

At LRTAP Workshop No. 4, Requirements for Mesoscale Acid Deposition Modelling and Monitoring in Western Canada (1985), a need for three types of models was identified: (1) urban photochemical,

(2) mesoscale deposition and (3) advanced complex deposition and oxidant. Important processes that often go unrepresented in such models were also identified as convective and frontal storms; flow in complex terrain; rain and snow scavenging; influences of soil particles; and cloud physics and chemistry. The Western Mesoscale Modelling Task Group (1985), which followed the workshop recommendations, added a fourth category of model types - statistical models - to provide for annual or seasonal loading estimates at more reasonable cost. The Task Group reviewed more than 100 available models, made the selections shown in Table 4, and recommended a multi-year program to implement the models, establish and maintain a data archive, apply the models to specific situations of interest, answer generic questions, compare outputs with observations, identify potential problem areas and, if necessary, design a field study for model verification.

Table 4. Models selected for use in Alberta and Western Canada.

Application Type	Mathematical Frame of Reference	
	Lagrangian	Eulerian
Urban photochemical	PLMSTAR	AIRSHED
Mesoscale deposition	MESOPUFF II	RTM III
Advanced complex		ADOM
Statistical	OME-STATMOD	FISHER RCDM

4.2.3 Long Range (greater than 1000 km)

As part of Western Canada acid deposition monitoring activities, the Atmospheric Environment Service of Environment Canada

applied their long range transport model to the impact of western North America sources upon several Alberta sites (Kociuba et al. 1984). Wet deposition of sulphur in Alberta was found to be 1 to 2 $kg \cdot ha^{-1} \cdot yr^{-1}$ of which about 60% was due to the assumed background. The predicted values were all smaller than those observed. Total deposition at Alberta sites ranged from 2.1 to 6.7 $kg \cdot ha^{-1} \cdot yr^{-1}$, the wet component accounting for 23% of the larger figure and 51% of the smaller figure.

5. SUMMARY

For sound environmental management, the integration of measurements, monitoring data, and modelling forecasts is essential. Fragmented information from Alberta research studies and monitoring programs has become available over the years, but integrated studies such as the Acid Deposition Research Program (ADRP) are needed. Models used to predict air quality and deposition in Alberta have yielded somewhat different results which, due to the paucity of long-term, representative measurements and monitoring data, cannot be verified. A unified data base is required to apply and test available models. Modifications of existing models to incorporate mesoscale processes, and development of environmental response models are needed. Further measurements of the atmospheric concentration and deposition velocities are required to determine the amount of dry deposition of gases and aerosols. Information is required concerning the contribution of windblown dust to total deposition. These needs in the measurement, monitoring and modelling of atmospheric pollutants will assist in the development of deposition standards/guidelines.

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